

## DEVELOPMENT OF NOVEL, MASS SPECTROMETRIC COMBUSTION MONITORING TECHNIQUES

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### ABSTRACT

An on-line gas and vapor analysis method has been developed to monitor combustion products by short column ("transfer line") Gas Chromatography/Mass Spectrometry. An automated vapor sampling inlet with only inert materials (quartz and fused silica) in the sample path is utilized to introduce flue gases into a 1 m long "transfer line" capillary GC column for rapid, repetitive chromatographic separation of products. The column effluent is introduced directly into the source of an ion trap type mass spectrometer. Combustion products from a gas fired rotary kiln were monitored by this method using a standard Ion Trap Detector (ITD). Detection limits of 20 to 50 ppb were obtained for various substituted benzenes. Monitoring of polycyclic aromatic hydrocarbons (PAHs) from the thermal desorption of contaminated soils in a fixed bed reactor utilized a modified Ion Trap Mass Spectrometer (ITMS). Varying isothermal column temperature allowed analysis of PAHs from naphthalene through 6 ring PAHs. The ITMS system provides higher sensitivity (~4 ppb for benzene) in addition to tandem MS and chemical ionization capabilities for unambiguous identification of combustion products incompletely resolved by the transfer line GC approach.

### INTRODUCTION

With the decreasing availability of hazardous waste disposal landfills, new technologies must be utilized for the permanent and proper elimination of these wastes. Of the approximately 265 million metric tons (MMT) of hazardous wastes generated yearly in the United States, at least 47 MMT per year could be incinerated [1]. In addition to the yearly generation of hazardous waste, the cleanup of uncontrolled hazardous waste sites must also be considered. The National Priority List (NPL) contains nearly 1000 sites which have been identified as hazards to public health and the environment and must be remediated. In addition there are estimated to be 10,000 sites which are presently uncontrolled [2]. Among the as yet uncontrolled sites are the widespread contaminated soils of former coal gas plant sites [3]. At these sites one may expect to encounter a broad range of polynuclear aromatic hydrocarbons (PAH's).

The importance of incineration technology for primary treatment of various types of industrial, medical, urban and agricultural waste as well as for remedial treatment of toxic waste dumps, landfills, chemical stockpiles, or accidental spill sites is widely recognized. Thermal treatment

is presently an effective way of removing organic contaminants from soil [4]. Generally, a two stage process is used in which the first stage is represented by a fixed bed or rotary kiln reactor [5] in which the organic contaminants are desorbed and/or pyrolyzed followed by a second stage, high temperature "afterburner" in which the volatile products of the first stage are effectively destroyed. Especially, the heaviest PAH components are likely to desorb very slowly from the soil matrix.

Continuous monitoring is needed to ensure that the incineration or thermal desorption system is operating properly at any given time [6]. Currently, unwanted emissions due to faulty equipment or operational procedures are generally detected (if at all) weeks or even months after the fact, when laboratory test data become available. Modern, on-line chromatographic and spectroscopic monitoring techniques offer the potential of near instantaneous feedback, thereby enabling immediate detection and correction of problems before significant levels of unwanted emissions have occurred. In view of their high sensitivity, specificity and speed, mass spectrometric methods play an important role among candidate monitoring techniques.

As shown by McClennen et al. [7,8] and Arnold et al. [9,10] a transfer line gas chromatography/mass spectrometry (TLGC/MS) technique, using the heated 1 m long coated fused silica capillary transfer line of a Finnigan-MAT Ion Trap Detector (ITD) as a short GC column, constitutes a powerful detection and characterization method for volatiles evolving from combustion reactors. In combination with a specially developed direct vapor sampling inlet [10] vapor detection levels in the low ppb range, corresponding to subpicogram quantities, can be achieved on an array of volatiles.

## EXPERIMENTAL

The transfer line chromatography is performed using a 1 m fused silica capillary column which is contained and heated in the ITD transfer line. The inlet of the column is at ambient pressure, while the exit is evacuated in the ion trap. Using a .18 mm ID column, the carrier gas (helium) velocity is  $2.7 \text{ m sec}^{-1}$  (at 4400 ft elevation), which is close to optimum for the column length and pressure drop.

For both the fixed bed and kiln experiments a direct vapor sampling transfer line GC/MS method was used. The direct atmospheric vapor sampling inlet, shown in Figure 1, consists of three concentric tubes with appropriate flow control plumbing and electronics. The inlet system is made from deactivated fused silica, quartz and glass, or glass lined metal tubing. The sample path contains no moving parts. When sampling, the gas is exposed to the column inlet for a controlled period of time (0.5 to 2 s) while 30 to 200  $\mu\text{L}$  of sample is admitted to the column. Helium carrier gas flow is then restored for the rest of the sampling cycle and GC separation of the sample takes place.

This inlet is coupled to fixed a pressure column drop transfer line chromatography. The 1 m long transfer line fused silica capillary GC column, provides both a nominal GC separation of components and a pressure drop to the ion source of the mass spectrometer. With the fixed pressure drop, the chromatographic conditions are controlled primarily by the column length, radius and temperature [11].

This transfer line inlet system was used with both a regular Finnigan MAT ITD and a modified ITMS system (termed MINITMASS) with axial modulation and Selective Mass Storage to allow for tandem mass spectrometry [12]. In addition to tandem capabilities, this second system permitted higher flow rates by using the axial modulation feature. The combination of increased resolution and increased flow rates resulted in higher sensitivity.

**Rotary Kiln** - The (GC/MS) system was used to monitor the evolution of trace amounts of hydrocarbons evolving from a material combusted in a rotary-kiln simulator. The rotary-kiln simulator is a useful tool for determining the transient emission of hydrocarbons from a control volume of waste. The simulator replaces the variable of kiln distance in a full-scale incinerator for that of time in the simulator; hence, the gas-phase concentrations of hydrocarbons are given as a function of combustion time for various combustion parameters. Approximately 11 g samples of a polymeric material were loaded into the kiln and incinerated at two different temperatures, 600 C and 760 C.

Rapid on-line analysis of rotary kiln combustion was obtained using the ITD based system. A sample flow of 25-50 ml/min of kiln gases were sampled from the transition area to the afterburner (see Figure 2). Samples were taken at 10 sec intervals to follow the concentration fluctuations following sample introduction into the kiln. The transfer line column was a 1 m long, .15 mm ID methyl silicone (DB-1) coated capillary column. The film thickness was 1.2  $\mu$ m thick and for the present results the column was operated at ambient and 82 C. Carrier gas flow conditions were 250 cm/s or 1.7 ml/min. For these analyses the mass spectrometer was scanned at 3 scans/second from m/z 35 to 120 for the ambient column temperature runs and from m/z 50 to 148 for the 82 C runs.

**Bed Characterization Reactor** - The bed characterization reactor (BCR, see Figure 3) is used to study the thermal desorption of compounds from contaminated soils and is described in detail elsewhere [13]. Contaminated and uncontaminated clay soil samples were obtained from several undisclosed sites. The contaminated samples were air dried and designated simply as "soil A" and "soil B." Approximately 200 grams of soil were placed beneath the BCR radiant heaters with a 3 cm/sec gas stream flowing across the bed, and were monitored for temperature change and weight loss. The exhaust gas was monitored 25 cm beyond the bed by a quartz tube drawing ~25 ml/min of gas past the vapor inlet. Samples of these gases were taken at 60 sec intervals to monitor the release of volatiles from the soil. The transfer line separation was performed using a 1 m long, .18 mm ID methyl-phenyl silicone (DB-5) coated capillary column. A .4  $\mu$ m thick stationary phase provided the separation of compounds in vapor phase. The larger column ID had carrier gas flows of 360 cm/sec or 3.5 ml/min. The modified ITMS (MINITMASS) system accommodated these higher flows with axial modulation. The spectra were scanned from m/z 50 to 200 or m/z 60 to 300 depending on the compounds of interest. Various boiling point ranges of compounds from naphthalene to 6 ring PAHs were monitored by isothermal operation of the transfer line at 125 or 230 C.

## RESULTS AND DISCUSSION

Figure 4 shows the chromatograms for repetitive GC/MS sampling of the kiln exhaust gases at 10 s intervals as indicated; the column temperature was 82°C and the kiln temperature was 600°C. The top trace represents the total ion chromatogram while selected chromatograms of ions with mass to charge ratios (m/z) 78 and 92 show the individual peaks for benzene and toluene, respectively. Note that the chromatogram of Figure 4 consist of a series of short chromatograms with peak areas of the separate compounds being proportional to the exhaust gas concentrations at each sampling time. Higher boiling compounds which do not elute within the 10 s sampling interval overlap with subsequent sampling, but can still be resolved by separate ion chromatograms and related back to the correct sample time.

Concentration profiles for separate compounds, determined by the GC/MS data illustrated in Figure 4, are shown in Figure 5 for a kiln temperature of 600 °C. The data show the concentrations (ppb) of benzene, toluene, C<sub>2</sub>-benzenes, phenol, and styrene as a function of time, with peaks at 30 s (20 s into combustion) and 85 s (75 s into combustion). The polymeric material would initially melt and pyrolyze, releasing high concentrations of organic compounds which then ignited and burned to form water and carbon dioxide. The two peaks in organic products came prior to the flame totally engulfing the samples, and after the local flame began to burn out. During higher temperature kiln tests, at 760 °C, only the most stable products such as benzene were observed above the 20-40 ppb detection limits as the organics were more quickly and completely oxidized.

Figure 6 shows the total ion chromatograms and several selected ion chromatograms for a single vapor analysis during BCR thermal treatment in N<sub>2</sub> of soil B. C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> alkylnaphthalene peaks are indicated by selected ion traces of m/z 142, 156, 170, respectively. For these vapor analyses, data were not acquired for the first 2 s after sampling to allow elution of the major gas and vapor components which were essentially non-retained on the GC column. With the short column operated isothermally at 125 °C, naphthalene was completely separated from the N<sub>2</sub> and other light gases while the combined phenanthrene/anthracene eluted less than 45 sec later.

By integrating the areas of specific molecular ion peaks within each 1 min segment, composite evolution curves were produced such as those shown for soil B in the BCR in Figure 7. Figure 7a compares the time evolution profiles for naphthalene at m/z 128, the combined phenanthrene/anthracene peaks at m/z 178, and their methyl homologs at m/z 142 and 192 respectively. In all cases a major evolution maximum is observed at approximately 10 minutes followed by a second minor peak at approximately 45 minutes into the run. The second evolution peak is larger relative to the first peak for the unsubstituted compounds than for the methyl homologs. In other words, a larger proportion of methyl homologs desorbed within the first 30 minutes or so when water is being desorbed from the soil bed.

The desorption of tar components from the BCR soil bed is further represented in Figure 7b where the heteroatomic compounds dibenzofuran at m/z 168, and dibenzothiophene at m/z 184, are compared to the PAH fluorene at m/z 166. As expected, the higher boiling dibenzothiophene (b.p. 332-333) has a slightly broader and later second peak than the dibenzofuran (b.p. 287). However, both of these have much larger second evolution peaks than the fluorene, similar to unsubstituted PAHs relative to their methyl homologs as in Figure 7a. One interpretation is that the four planar, fully aromatic compounds, namely naphthalene, phenanthrene/anthracene, dibenzofuran and dibenzothiophene, might be more strongly bound to the soil and less completely released in the first thermal desorption or "steam stripping" process than the alkyl substituted or non-planar (fluorene) compounds. A second possibility is that a larger fraction of the fluorene and methyl-aromatics might have reacted to form other products due to their greater ease of oxidation. This latter explanation is supported by the observation of aldehyde and ketone oxidation products such as 9-fluorenone in extracts from incompletely desorbed soils run at lower temperatures or shorter times.

## CONCLUSIONS

The broad range of boiling points and polarities of the organic vapors produced during incineration or the thermal treatment of contaminated wastes and soils mandates the use of sophisticated instrumentation for monitoring their production, evolution, and destruction, especially during the design of new facilities. The results of this work have demonstrated that the on-line, short-column GC/MS approach is capable of reliably obtaining qualitative and quantitative data on the products evolving from two types of incinerators.

The on-line short column GC/MS systems are shown to be powerful instruments for measurement of transient concentrations (30-60 sec interval) of a broad range of aromatic compounds. Short column gas chromatography separates the organic vapors away from the major ambient atmospheric constituents and also provides some separation of isomers indistinguishable by MS. The mass spectrometer provides a rapid and sensitive method of compound identification and specific quantitation. A standard Ion Trap Detector is an economical MS system with 20-40 ppb detection limits for aromatics while the MINITMASS system offers improved sensitivity and the added selectivity of MS<sup>n</sup> capability.

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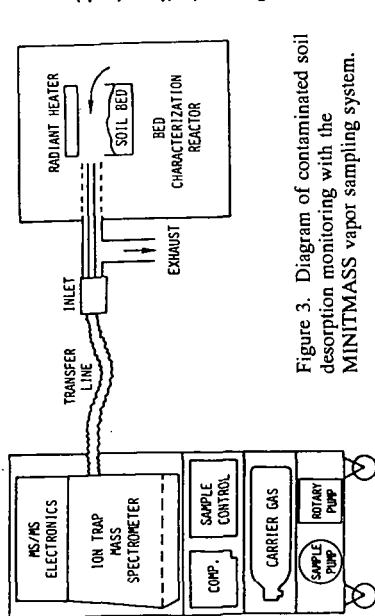


Figure 3. Diagram of contaminated soil desorption monitoring with the MINITMASS vapor sampling system.

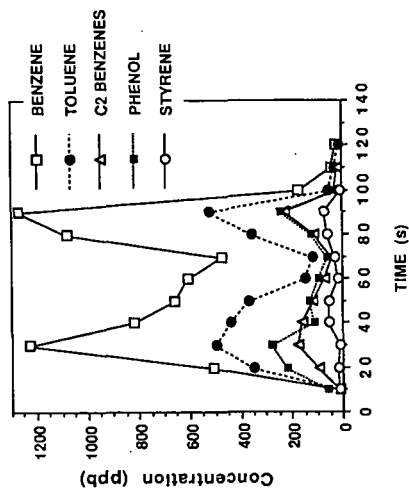


Figure 5. Time evolution of organic compounds during incineration of medical supplies at 600 C in a rotary kiln simulator.

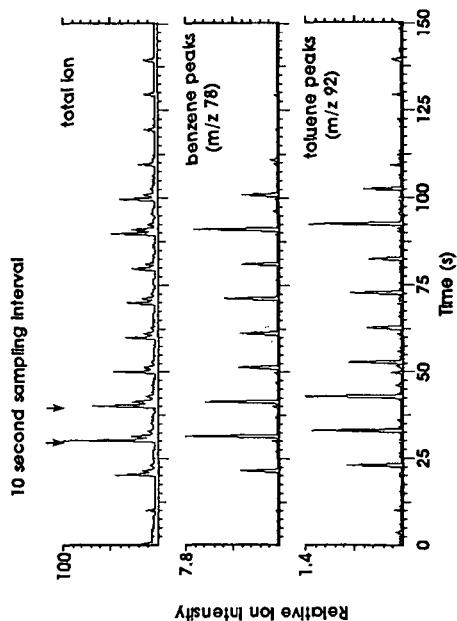


Figure 4. Total and selected ion chromatograms from 16 repetitive GC/MS vapor samples during incineration of disposable medical supplies in the rotary kiln simulator.

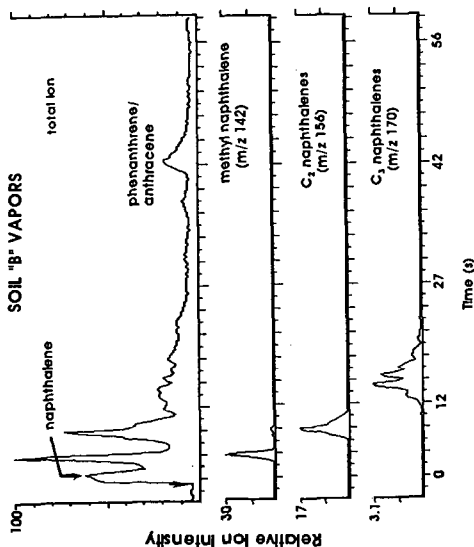


Figure 6. Total and selected ion chromatograms for a single on-line vapor sample GC/MS analysis during a 400 °C BCR run on soil B.

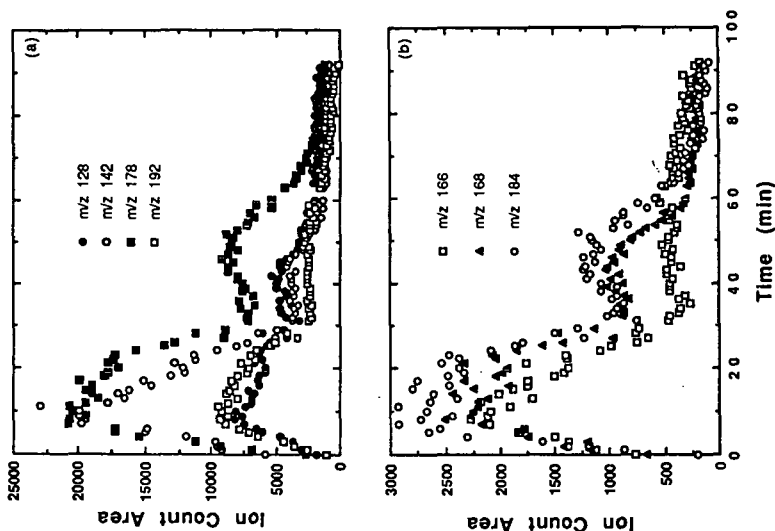


Figure 7. Time evolution profiles for several compounds from vapor sampling of the thermal treatment of soil B in the BCR at 400 °C. Each point is from the integrated area of a specific peak in the molecular ion chromatogram for the 90 vapor samples. The ions represented are: in a) m/z 128, naphthalenes; m/z 142, methyl-naphthalenes; m/z 178, phenanthrene/anthracene; m/z 192, methyl-phenanthrenes and anthracenes; in b) m/z 166, fluorene; m/z 168, dibenzofuran; and m/z 184, dibenzo thiophene.

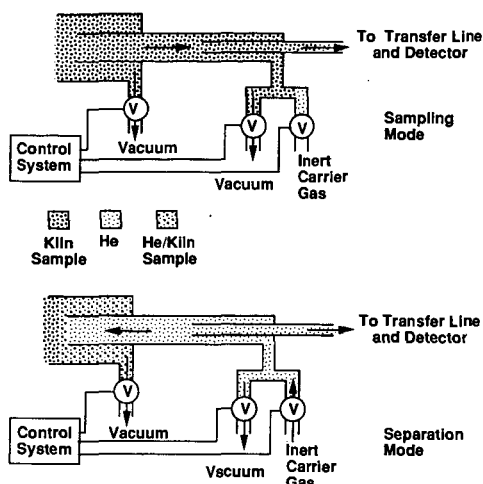


Figure 1. Schematic diagram of vapor sampling inlet operation.

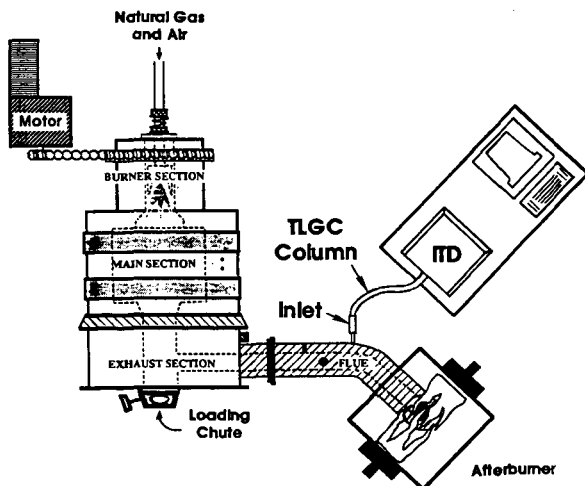


Figure 2. Top view of rotary kiln simulator with on-line GC/MS system using an Ion Trap Detector (ITD).